

Structure of a Schiff-Base Macrocyclic Containing Convergent Methoxy Groups

BY P. BARET, W. MONETA AND J. L. PIERRE

Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Université de Grenoble I, BP 68,
38402 Saint Martin d'Hères CEDEX, France

AND M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie du CNRS associé à l'Université de Grenoble I, BP 166X,
38042 Grenoble CEDEX, France

(Received 2 September 1987; accepted 24 March 1988)

Abstract. $C_{38}H_{40}N_4O_4$, 35,36,37,38-tetramethoxy-8,12,25,29-tetraazapentacyclo[29.3.1.1^{2,6}.1^{14,18}.1^{19,23}]-octatriaconta-1(35),2,4,6(38),7,12,14,16,18(37),-19,21,23(36),24,29,31,33-hexadecaene, $M_r = 616.73$, orthorhombic, $C2cb$ (C_{2v}^1), $a = 10.941$ (9), $b = 21.46$ (2), $c = 14.53$ (1) Å, $V = 3412$ (8) Å³, $Z = 4$, $D_x = 1.198$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.085$ mm⁻¹, $F(000) = 1312$, $T = 293$ K, final $R = 0.055$ for 1431 independent reflexions. The diphenyl units act as chiral barriers and the macrocyclic molecule assumes a (\pm)-configuration. The dihedral angle between the two benzene rings of the diphenyl moiety is 66.5°. The four O atoms are located at the corners of a tetrahedron, providing potentially convergent ligand sites for complexation.

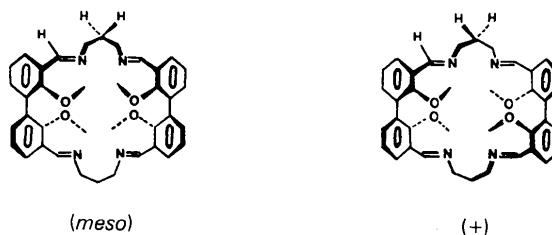
Introduction. Host-guest chemistry, which mimics biological complexation, has been a matter of wide interest during the past decade. The literature is rich in descriptions of macrocyclic ligand systems synthesized to complex metal ions (Melson, 1979).

The cavities of most of these hosts are defined so that the macrocycle's binding sites can adapt to the propensities of potential metal-ion guests. Hosts with preorganized cavities of shapes complementary to a variety of guests have been designed, synthesized and examined (Cram, 1986).

The macrocyclic ligands that we have designed provide a hydrophilic intramolecular cavity, involving two rigid 1,1'-biaryl subunits substituted in the 2,2'-positions with hydroxyl or methoxyl groups. Two diimino or diamino bridges join the 3 and 3' positions respectively. These macrocyclic structures are based on two tetradentate Schiff-base subunits of the 'SALEN' type and are also comparable with the chorand hosts described by Cram's group.

Aryl units and their attached atom ordinarily are coplanar and tend to rigidify molecules of which they are a part; biaryl units are chiral and possess enforced conformations that provide hosts with desired symmetry properties. The compounds of this study combine

two like chiral axes and therefore should exist either as enantiomers (containing C_2 axis) or as a *meso* isomer (containing a mirror plane).



This paper reports the crystal and molecular structure of a tetramethoxy derivative possessing a $(CH_2)_3$ bridge. This compound is the kinetic product of the synthesis.

Experimental. The synthesis and the characterization of the Schiff-base macrocycles are described elsewhere (Moneta, Baret & Pierre, 1985, 1988).

Density not measured. Prism fragment $0.25 \times 0.25 \times 0.25$ mm. Nonius CAD-4 diffractometer, graphite monochromator.

Systematic absences: hkl ($h + k = 2n$), $h0l$ ($l = 2n$), $hk0$ ($h = 2n$). 25 reflexions ($10 < \theta < 15^\circ$) for refining unit-cell dimensions. ω - 2θ scan. 2575 reflexions measured ($3 < \theta < 30^\circ$), hkl , $h_{\max} = 14$, $k_{\max} = 30$, $l_{\max} = 19$. Scan width 1.20° , scan speed variable between 0.04 and $0.02^\circ \text{ s}^{-1}$, total background measuring time between 15 and 30 s. Two orientation ($4,12,0$ and $\bar{4},12,0$) and two intensity ($4,\bar{1}2,0$ and $\bar{4},\bar{1}2,0$) reference reflexions with no significant variation. Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods (MULTAN77; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement with 1431 reflexions corresponding to $I > 2\sigma_I$. Final $R = 0.055$ ($wR = 0.050$). No extinction correction. $S = 0.528$. Max. $\Delta/\sigma = 0.15$ [x of H(3)].

Table 1. Final atomic coordinates for $C_{38}H_{40}N_4O_4$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \cdot \beta_{ij}$$

	x	y	z	B_{eq} (\AA^2)
O(1)	-0.0860 (4)	0.0955 (2)	0.5394 (2)	10.7 (1)
O(2)	0.108* (4)	0.0190 (1)	0.6433 (2)	7.56 (8)
N(1)	0.0328 (4)	-0.0687 (2)	0.8787 (2)	5.56 (7)
N(2)	-0.0504 (4)	0.1834 (2)	0.2976 (2)	5.85 (8)
C(1)	-0.0648 (5)	-0.1714 (2)	0.8705 (2)	5.73 (9)
C(2)	0.8719 (4)	0.8376 (2)	0.7783 (3)	6.0 (1)
C(3)	-0.0517 (5)	0.1527 (2)	0.3697 (2)	5.73 (9)
C(4)	0.0238 (4)	0.1685 (2)	0.4511 (2)	5.01 (8)
C(5)	0.1151 (4)	0.2119 (2)	0.4451 (2)	5.20 (8)
C(6)	0.1869 (5)	0.2259 (2)	0.5196 (3)	6.2 (1)
C(7)	0.1667 (5)	0.1946 (2)	0.6023 (3)	5.8 (1)
C(8)	0.0753 (4)	0.1508 (2)	0.6105 (2)	5.23 (9)
C(9)	0.0040 (4)	0.1385 (2)	0.5350 (2)	5.36 (9)
C(10)	0.3155 (8)	0.3972 (5)	0.4184 (6)	16.2 (3)
C(11)	0.0552 (5)	0.1205 (2)	0.7016 (2)	5.69 (9)
C(12)	0.0181 (6)	0.1562 (2)	0.7763 (2)	6.8 (1)
C(13)	-0.0003 (6)	0.1287 (2)	0.8614 (3)	7.6 (1)
C(14)	0.0167 (5)	0.0663 (2)	0.8739 (2)	6.4 (1)
C(15)	0.0541 (4)	0.0284 (2)	0.8008 (2)	5.18 (8)
C(16)	0.0732 (4)	0.0570 (2)	0.7153 (2)	5.11 (8)
C(17)	0.2389 (7)	0.0203 (4)	0.6274 (6)	14.5 (2)
C(18)	0.0725 (4)	-0.0383 (2)	0.8104 (2)	5.16 (8)
C(19)	0.0532 (5)	-0.1362 (2)	0.8785 (2)	5.64 (9)

* x of O(2) fixed at 0.108.

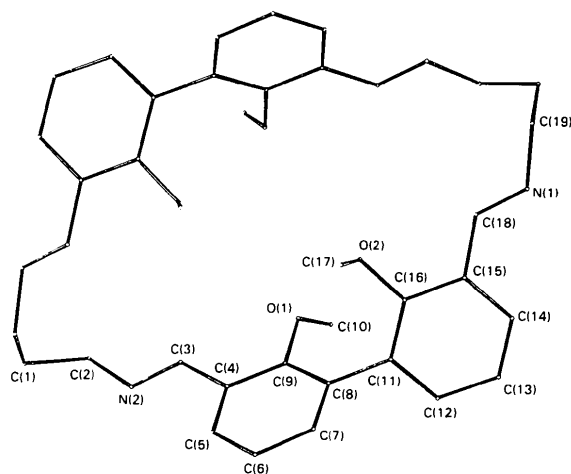
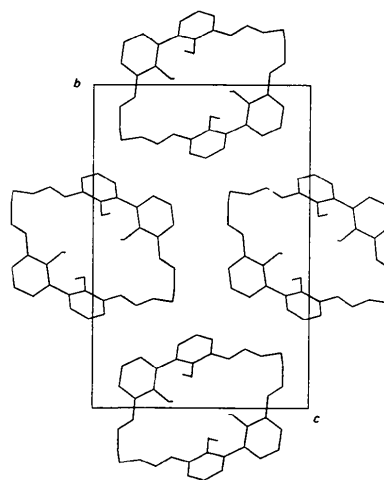
Table 2. Main interatomic distances (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) in $C_{38}H_{40}N_4O_4$

O(1)—C(2)	1.520 (9)	C(19)—C(1)—C(2)	113.3 (6)
O(1)—C(19)	1.500 (10)	C(1)—C(2)—N(3)	111.2 (6)
C(2)—N(2)	1.463 (9)	C(2)—N(2)—C(3)	117.9 (6)
N(2)—C(3)	1.237 (7)	N(2)—C(3)—C(4)	123.1 (7)
C(3)—C(4)	1.483 (9)	C(3)—C(4)—C(5)	120.8 (5)
C(4)—C(5)	1.368 (8)	C(3)—C(4)—C(9)	120.3 (6)
C(4)—C(9)	1.396 (7)	C(5)—C(4)—C(9)	118.9 (6)
C(5)—C(6)	1.372 (10)	C(4)—C(5)—C(6)	121.1 (6)
C(6)—C(7)	1.395 (9)	C(5)—C(6)—C(7)	119.0 (8)
C(7)—C(8)	1.377 (10)	C(6)—C(7)—C(8)	121.2 (7)
C(8)—C(11)	1.492 (7)	C(7)—C(8)—C(9)	118.3 (5)
C(8)—C(9)	1.373 (8)	C(7)—C(8)—C(11)	118.8 (6)
C(9)—O(1)	1.352 (9)	C(11)—C(8)—C(9)	122.9 (6)
O(1)—C(10)	1.25 (2)	C(8)—C(9)—O(1)	120.5 (5)
C(11)—C(12)	1.389 (8)	C(8)—C(9)—C(4)	121.5 (6)
C(11)—C(16)	1.391 (8)	C(4)—C(9)—O(1)	118.0 (6)
C(12)—C(13)	1.386 (9)	C(10)—O(1)—C(9)	124 (1)
C(13)—C(14)	1.364 (10)	C(8)—C(11)—C(12)	119.7 (5)
C(14)—C(15)	1.399 (8)	C(8)—C(11)—C(16)	122.2 (5)
C(15)—C(16)	1.402 (7)	C(12)—C(11)—C(16)	118.1 (5)
C(16)—O(2)	1.379 (6)	C(11)—C(12)—C(13)	120.3 (6)
O(2)—C(17)	1.45 (1)	C(12)—C(13)—C(14)	121.1 (6)
C(18)—N(1)	1.265 (7)	C(13)—C(14)—C(15)	120.6 (6)
N(1)—C(19)	1.467 (8)	C(14)—C(15)—C(18)	122.7 (5)
C(19)—C(1)—C(2)—N(2)	-88.1 (3)	C(14)—C(15)—C(16)	117.6 (5)
C(1)—C(2)—N(2)—C(3)	-6.8 (4)	C(16)—C(15)—C(18)	119.7 (5)
C(2)—N(2)—C(3)—C(4)	176.9 (4)	C(11)—C(16)—C(15)	122.3 (5)
N(2)—C(3)—C(4)—C(9)	169.5 (5)	C(11)—C(16)—O(2)	120.6 (5)
C(8)—C(9)—O(1)—C(10)	72.4 (8)	C(15)—C(16)—O(2)	117.1 (5)
C(9)—C(8)—C(11)—C(16)	66.5 (7)	C(16)—O(2)—C(17)	112.5 (8)
C(11)—C(16)—O(2)—C(17)	83.1 (6)	N(1)—C(18)—C(15)	122.4 (6)
		C(18)—N(1)—C(19)	117.1 (5)
		C(1)—C(19)—N(1)	111.5 (6)

Max. peak height in final difference-Fourier synthesis 0.17 e \AA^{-3} . Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) *SDP* used for all calculations. Computer used: VAX 780. Hydrogen atoms of the two $C(10)H_3$ and $C(17)H_3$ terminal groups could not be located.

Discussion. Table 1 reports the final atomic coordinates and Table 2 the main interatomic distances, bond angles and torsion angles.* Fig. 1 is an *ORTEP*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44892 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. *ORTEP* view of the macrocycle perpendicular to the A-ring plane.Fig. 2. Projection of the atomic arrangement along the a axis, between 0 and 0.5.

(Johnson, 1976) view of the molecule perpendicular to the *A* ring. Fig. 2 shows a projection of the atomic arrangement along the *a* axis.

Although the structure formulated in Fig. 1 possesses the (*S,S*)-configuration, the X-ray structure involved a racemate (Fig. 2). The (\pm)-isomer is configurationally stable at working temperatures; the *meso* form is not obtained in the synthesis.

The dihedral angle between the benzene rings in the biphenyl moiety is 66.5 (7)°. The methoxy groups occupy a down-up-down-up position, with the methyls diverging from the centre of the cavity. The four methoxy oxygens are at the corners of a tetrahedron, the distances being respectively O(1)···O(2) 3.078 (5), O(1)···O(2) 4.195 (5) Å, O(1)···O(1') 4.255 (9) Å. This arrangement should enhance the hydrophilicity of the cavity.

The imino groups adopt an *anti* conformation as shown in Fig. 1 with the dihedral angle C(4)–C(3)–N(2)–C(2) 176.9 (4)°.

The shape of the cavity may find some use in designing hosts for chiral recognition studies.

The authors are grateful to Dr Claudine Cohen-Addad and Dr Anne Renault for fruitful discussions. The X-ray data collection was performed within the 'Groupement Grenoblois de Diffractometrie'.

References

- CRAM, D. J. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 1039–1057.
 Enraf-Nonius (1977). *Structure Determination Package. RSX 11 M* version. Enraf-Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MELSON, G. A. (1979). *Coordination Chemistry of Macrocyclic Compounds*. New York: Plenum.
 MONETA, W., BARET, P. & PIERRE, J. L. (1985). *J. Chem. Soc. Chem. Commun.* pp. 899–901.
 MONETA, W., BARET, P. & PIERRE, J. L. (1988). In preparation.

Acta Cryst. (1988). **C44**, 1256–1262

Structures of Eight 2-Dialkylamino-6*H*-1,3-oxazin-6-ones

BY TULLIO PILATI

Centro per lo Studio delle Relazioni fra Struttura e Reattività Chimica, Via Golgi 19, 20124 Milano, Italy

(Received 11 December 1987; accepted 15 March 1988)

Abstract. (1): 2-Dimethylamino-6-oxo-4-phenyl-6*H*-1,3-oxazine-5-carbonitrile-0.5 dioxane solvate, C₁₃H₁₁N₃O₂·½C₄H₈O₂, *M_r* = 285.3, monoclinic, *P*2₁/*n*, *a* = 10.127 (3), *b* = 7.281 (1), *c* = 19.928 (3) Å, β = 98.26 (2)°, *V* = 1454.1 (5) Å³, *Z* = 4, *D_x* = 1.303 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.87 cm⁻¹, *F*(000) = 600, room temperature, final *R* = 0.065 for 2484 observed reflections. (2): 5-Benzoyl-2-dimethylamino-4-phenyl-6*H*-1,3-oxazin-6-one, C₁₉H₁₆N₂O₃, *M_r* = 320.3, triclinic, *P*1̄, *a* = 9.603 (1), *b* = 11.692 (2), *c* = 8.512 (1) Å, α = 92.01 (1), β = 110.76 (1), γ = 112.05 (1)°, *V* = 812.6 (2) Å³, *Z* = 2, *D_x* = 1.309 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.84 cm⁻¹, *F*(000) = 336, room temperature, final *R* = 0.043 for 2962 observed reflections. (3): Ethyl 2-dimethylamino-6-oxo-4-phenyl-6*H*-1,3-oxazine-5-carboxylate, C₁₅H₁₆N₂O₄, *M_r* = 288.3, monoclinic, *C*2/*c*, *a* = 15.909 (3), *b* = 10.711 (2), *c* = 17.087 (3) Å, β = 91.98 (1)°, *V* = 2909.9 (9) Å³, *Z* = 8, *D_x* = 1.316 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.90 cm⁻¹, *F*(000) = 1216, room

temperature, final *R* = 0.041 for 1887 observed reflections. (4): Ethyl 2-dimethylamino-6-oxo-5-phenyl-6*H*-1,3-oxazine-4-carboxylate, C₁₅H₁₆N₂O₄, *M_r* = 288.3, monoclinic, *P*2₁/*c*, *a* = 7.782 (1), *b* = 11.086 (2), *c* = 16.993 (4) Å, β = 97.68 (2)°, *V* = 1452.9 (5) Å³, *Z* = 4, *D_x* = 1.318 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.90 cm⁻¹, *F*(000) = 608, room temperature, final *R* = 0.040 for 2219 observed reflections. (5): 2-Morpholino-5-*o*-tolyl-6*H*-1,3-oxazin-6-one, C₁₅H₁₆N₂O₃, *M_r* = 272.3, monoclinic, *C*2/*c*, *a* = 19.321 (6), *b* = 15.868 (3), *c* = 9.113 (3) Å, β = 102.40 (3)°, *V* = 2729 (1) Å³, *Z* = 8, *D_x* = 1.326 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.87 cm⁻¹, *F*(000) = 1152, room temperature, final *R* = 0.044 for 2154 observed reflections. (6): Ethyl 2-diisopropylamino-6-oxo-6*H*-1,3-oxazine-5-carboxylate, C₁₃H₂₀N₂O₄, *M_r* = 268.3, monoclinic, *P*2₁/*n*, *a* = 12.128 (2), *b* = 9.836 (1), *c* = 12.981 (2) Å, β = 110.10 (1)°, *V* = 1454.2 (4) Å³, *Z* = 4, *D_x* = 1.225 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.85 cm⁻¹, *F*(000) = 576, room temperature, final